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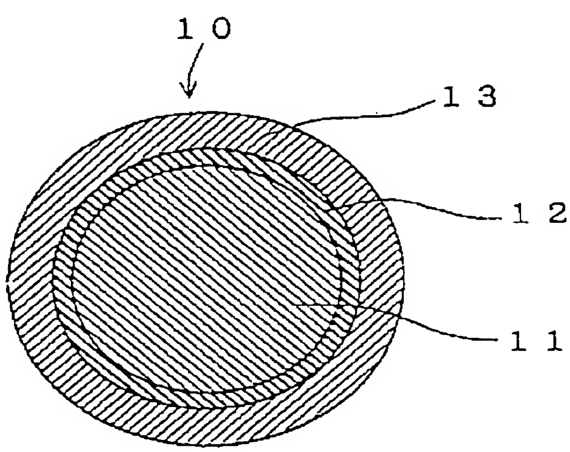
(54) Heat-proof electric wire comprising a benzimidazole-based polymer coating

(57) An insulating material comprised of a benzimidazole-based polymer layer and a fluorine-containing rubber layer is prepared. This material provides a heat-proof product, especially a heat-proof electric wire. To manufacture such a heat-proof wire, a varnish solution is prepared by dissolving benzimidazole-based polymers having a low degree of polymerization in a basic solvent, then adding a radical-polymerization initiator to this solvent. Subsequently an electric wire is soaked in this solution and baked, so that the applied benzimidazole-based polymers are cross-linked. By repeating this procedure, the electric wire is coated with a benzimidazole-based polymer layer (12, 24). This coated wire is further coated with a fluorine-containing rubber layer (13, 25) to obtain a heat-resistant electric wire (10, 20) that is also resistant to dielectric breakdown.

FIG_1



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Description

The present invention relates to a heat-proof insulating material, and a heat-proof electric wire coated therewith. The invention relates also to a method for preparing such insulating material and electric wire, as well as a method for using such products.

The method according to the invention is well adapted to manufacture an enamelled electric wire having a high heat resistance.

There already exist heat-proof electric wires such as polyimide coated wires, enamelled wires and highly heat-proof cementing enamelled wires. However, the maximal temperatures of use for these wires are respectively 250°C, 150 to 220°C and 220°C, the temperature limit being therefore 250°C at most.

Therefore, research is currently being carried out into a heat-proof electric wire having a high heat resistance, i. e. an electric wire resistant at temperatures above 250°C. The present inventors have already developed an electric wire coated with a film of benzimidazole-based polymer and filed a Japanese patent application No. Heisei 4 - 124 342. In this disclosure, a polymer PBI having high heat resistance was applied to a non-coated electric wire or an electric wire coated with an insulating layer, then the polymer was baked to form a benzimidazole-based polymer film or layer.

Such a PBI coated electric wire has a high heat resistance, showing a softening temperature above 350°C under heating. However, at high temperatures, it may be partially oxidized by air, so that, depending on the conditions of use, such a coated wire could not make full use of its advantageous features with respect to heat resistance, voltage resistance, flexibility or similar.

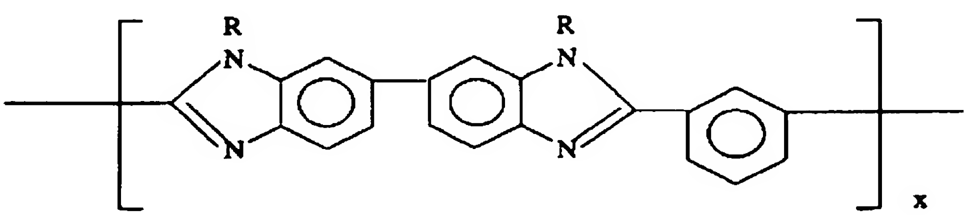
It is therefore an object of the present invention to improve the above-mentioned benzimidazole-based polymer-film-coated electric wire or the like, so as to obtain a heat-proof electric wire or insulating material that displays fully the advantageous characteristics proper to the polymer PBI, such as high heat resistance.

It is another object of the invention to provide usage methods for such electric wires or insulating materials, as well as a manufacturing processes thereof.

To this end, the invention provides a heat-proof insulating material comprising:

- a first layer comprised of benzimidazole-based polymer, the layer having a first face adapted to confront an element containing at least an electrically conductive part, and a second face; and
- a second layer comprised of a fluorine-containing rubber, the second layer being securely fixed to the second face of the first layer.

The first layer may comprise a product obtainable by crosslinking a plurality of benzimidazole-based polymers of formula (I):



(I)

where R is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms and x is an integer equal to, or above, 5, may be the same or different for each of the plurality of polymers, and is chosen to yield solvent-soluble polymers. The maximum value of x is about 3,500.

The fluorine-containing rubber may comprise a product obtainable by polymerizing a selection of at least one of the monomer groups of a, b and c represented by formula (II):

$$
\overset{a}{l\left[\begin{array}{cc} R_1 & R_3 \\ | & | \\ C & = C \\ | & | \\ R_2 & R_4 \end{array}\right]}
\qquad
\overset{b}{m\left[\begin{array}{cc} R_1' & R_3' \\ | & | \\ C & = C \\ | & | \\ R_2' & R_4' \end{array}\right]}
\qquad
\overset{c}{n\left[\begin{array}{cc} R_1'' & R_3'' \\ | & | \\ C & = C \\ | & | \\ R_2'' & R_4'' \end{array}\right]}
\qquad (II)
$$

where l, m and n indicate respectively the total number of monomers constituting each group of a, b or c, each of l, m and n ranging from 20 to 200,000; at least one member, chosen from a set consisting of those of R1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3'' and R_4'' which are included in said selection of at least one of the monomer groups, is a fluorine atom, the other members of said set being chosen from the group consisting of a hydrogen atom, a fluorine atom, a chlorine atom, a substituted or non-substituted methyl group and an O-R_5 group, where R_5 is chosen from the group consisting of a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a cyclohexyl group, a cyclohexyl group substituted by lower alkyl groups having 1 to 4 carbon atoms, a hydroxyalkyl group having 1 to 8 carbon atoms, an aminoalkyl group having 1 to 8 carbon atoms, a dialkylaminoalkyl group having 1 to 8 carbon atoms, a glycidyl group, a tetrahydrofuran group, a tetrahydrofuran group substituted by lower alkyl groups having 1 to 4 carbon atoms, a benzyl group, a group $(-CH_2CH_2-O-)tCH_2CH_2OH$ where t is a positive integer in the range of 1 to 10, and a group R_6-N-R_7 where each of R_6 and R_7 is either a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

The heat-proof insulating material according to the invention may contain simultaneously a first layer comprised of the product obtainable by cross-linking benzimidazole-based polymer of formula (I) and a second layer comprised of the fluorine-containing rubber comprising a product obtainable by polymerizing a selection of at least one of the monomer groups represented by formula (II).

The element containing at least an electrically conductive part may be either an electric wire or an electric wire coated with an insulating layer.

The invention provides also a heat-proof electric wire comprising:

- a wire portion containing at least an electrically conductive part;
- a first layer comprised of benzimidazole-based polymer, said layer circumferentially coating the wire portion; and
- a second layer comprised of a fluorine-containing rubber, the second layer circumferentially coating the first layer,

the wire portion, the first layer and the second layer being securely fixed.

In this heat-proof electric wire, the first layer may be obtained by crosslinking the benzimidazole-based polymers having the formula (I). Independently of the composition of the first layer, the fluorine-containing rubber of the second layer may comprise a product obtainable by polymerizing at least one of the monomer groups shown in the formula (II). However, the electric wire can also combine the first layer containing the cross-linked product of benzimidazole-based polymers of formula (I) with the second layer comprising a product obtainable by polymerizing at least one of the monomer groups represented by formula (II).

Preferably, the wire portion containing at least an electrically conductive part is an electric wire.

It can also be an electric wire coated with an insulating layer.

Further, the present invention provides a method for manufacturing a heat-proof insulating material comprising; a first layer comprised of benzimidazole-based polymer, the layer having a first face adapted to confront an element containing at least an electrically conductive part, and a second face; and a second layer comprised of a fluorine-containing rubber, the method comprising the steps of:

a) dissolving benzimidazole-based polymers having a low degree of polymerization in a basic solvent, thereby obtaining a varnish solution containing the benzimidazole-based polymers;
b) adding a radical-polymerization initiating agent to this solution, thereby obtaining a mixture solution;
c) extending the mixture solution into a shape corresponding to the surface of the element to be confronted;
d) baking the mixture solution, whereby the benzimidazole-based polymers are heat cross-linked, thereby forming a first layer having a first face adapted to confront said element, and a second face;
e) repeating, where appropriate, steps a) to d) thereby reinforcing the first layer; and
f) coating the second face of the first layer with a second layer comprised of a fluorine-containing rubber so as to be secured on the first layer.

There is also provided a method for manufacturing a heat-proof electric wire comprising; a wire portion containing at least an electrically conductive part; a first layer comprised of benzimidazole-based polymer, the layer circumferentially coating the wire portion; and a second layer comprised of a fluorine-containing rubber, the second layer circumferentially coating the first layer, the method comprising the steps of:

a) dissolving benzimidazole-based polymers having a low degree of polymerization in a basic solvent, thereby obtaining a varnish solution containing benzimidazole-based polymers;
b) adding a radical-polymerization initiating agent to this solution, thereby obtaining a mixture solution;
c) applying the mixture solution to the circumferential surface of the wire portion;
d) baking the mixture solution, whereby the benzimidazole-based polymers are heat cross-linked, thereby forming a first layer securely on the wire portion;
e) repeating, where appropriate, steps a) to d), thereby reinforcing the first layer; and
f) coating the first layer with a second layer comprised of a fluorine-containing rubber so as to be secured on the first layer.

Preferably, the coating mentioned in step f) is effected by extrusion. Further, during the extrusion, the second layer may be pressed onto the first layer from the exterior through pressurized gas thereby obtaining a better adhesion between the two layers.

The heat-proof electric wire thus manufactured may be used in an aircraft, for high voltage cables, communication cables, electrical heaters or similar.

The above and other objects, features and advantages of the invention will be made apparent from the following description of the preferred embodiments, given as a non-limiting example, with reference to the accompanying drawings, in which:

- figure 1 shows a transversal cross-sectional view of a heat-proof electric wire according to the invention, manufactured from a non-coated electric wire;
- figure 2 shows a transversal cross-sectional view of a heat-proof electric wire according to the invention, manufactured from an electric wire coated with an insulating layer;
- figure 3 shows schematically a process for applying a benzimidazole-based polymer coating; and
- figure 4 shows an example of a process for applying a fluorine-containing rubber coating.

Figure 1 shows a heat-proof electric wire 10 wherein a non-coated electric wire 11 as a conductor is covered with a film or layer 12 comprised of benzimidazole-based polymer (hereinafter referred to as PBI).

Further, the PBI film 12 is covered with a coating 13 comprised of a fluorine-containing rubber. The PBI film 12 confers a high heat resistance, whilst the coating 13 enables the PBI film 12 to maintain this feature by preventing it from contact with air and subsequent air oxidation.

A thus configured heat-proof electric wire 10 may be used as electric wires for aircrafts, for high voltage application, for communication or for electrical heaters that require high heat resistance.

The heat-proof electric wire 10 is prepared by taking the following basic steps: firstly, PBI compounds having a low degree of polymerization are dissolved in a specific solvent, thereby preparing a PBI varnish. During the varnish preparation, radical-polymerization initiating agents are also added. The solvent for varnish preparation may include a basic solvent such as dimethylacetamide (DMA), dimethylformamide (DMF), pyridine, etc., or hydrogen-bonding shielding solvents such as dimethylsulphoxide (DMSO) etc.

The PBI concentration in the varnish solution may vary from 1% to 80%, but preferably from 5% to 40%.

The radical-polymerization initiating agent may be, for example, benzoyl peroxide, or lauroyl peroxide, di-t-butyrophthalate peroxide, azo-bis-isobutyronitrile (AIBN), phenylazoalkylsulphonic acid, N-nitroso-N-acyl compound, or the like.

The radical-polymerization initiator is added to the PBI varnish, in order to neutralize polymerization-inhibiting agents present in DMA etc. to be used as varnish solvent. This addition may promote the cross-linking reaction of PBI, occurring during the hereinafter mentioned baking treatment, and form a sufficiently strong PBI film.

To form a cross-linked PBI layer, it is necessary to bake the layer at temperatures above 410°C. However, in this temperature zone, a cross-linking and a oxidative decomposition occur concurrentially, so that a delicate PBI-molecular stacking is required.

Usually, in the low molecular weight region, the stacking between PBI molecules seems to be insufficient, with the result that to strengthen the layer by a mere baking is sometimes very difficult.

To solve this problem, it is very effective to add a radical polymerization initiator such as AIBN. Infrared (IR) analysis suggests that the initiator AIBN not only neutralizes inhibitors in the basic solvents but also reinforces the molecular stacking, thereby contributing to PBI heat cross-linking.

The PBI varnish, with the added radical-polymerization initiator, is applied to the surface of a non-coated electric wire and adhered thereto by baking. The baking treatment usually consists in repeating the varnish application and baking. Figure 3 shows a practically used device consisting of a baking furnace 1, an applying unit 2, a continuous annealing furnace 3 and a coiling unit 4. In this device, a wire 5 such as an electric conductor, a coated electric wire etc., wound on the coiling unit 4, is uncoiled therefrom, annealed in the continuous annealing furnace 3, sent to the applying unit 2 and applied with the varnish, then sent to the baking furnace 1 where the varnish is adhered to the wire by baking.

Further, the varnish baked wire 5 is processed repeatedly through the applying unit 2 and the baking furnace 1, thereby repeatedly receiving the varnish application and the baking. The wire coated with the PBI film is then recovered from a delivering unit 6.

There are no particular limitations on the kind and diameter of conductors or non-coated wire or on the thickness of the coating in this invention.

In accordance with typical handling processes, when the non-coated electric wire 11 has a diameter less than 0.6 mm, the applying unit may be a horizontal furnace, whilst, when the diameter is larger than 0.6 mm, a vertical furnace may be used.

This principle may be applied for the PBI coating and baking of the present invention, by choosing the type of furnace depending on the circumstances. One may also appropriately modify the application frequency, the baking temperature, the applying speed, etc. according to the type of paint or varnish to be baked, the type of baking furnace, etc.

The application frequency (number of coatings) may vary from once to several hundred times but more appropriately from twice to 20 times.

The baking temperature may be chosen from between room temperature and 1000°C but preferably between 500°C and 800°C.

As has been seen, the electric wire is covered with the PBI film 12. Then, the outer surface of the film is further covered with the fluorine-containing rubber, thereby forming another coating 13. Such a fluorine-containing rubber is comprised of a polymer obtainable from a selection of the monomer groups having the formula (II) which may be, for example, polytetrafluoroethylene (PTFE), a copolymer of tetrafluoroethylene and hexafluoropropylene (FEP), a copolymer of tetrafluoroethylene and perfluoroalkylvinylether (PFA), a copolymer of tetrafluoroethylene, hexafluoropropylene and perfluoroalkylvinylether (EPE), a copolymer of ethylene and tetrafluoroethylene (ETFE), polychlorotrifluoroethylene (PCTFE), a copolymer of ethylene and chlorotrifluoroethylene (ECTFE), polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), etc.

Processes for preparing such a fluorine-containing rubber coating include Physical Vapor Deposition (PVD) method, Chemical Vapor Deposition (CVD) method, an extrusion method etc.

When the extrusion method is applied, the extrusion device typically will comprise a barrel 31, a cylinder 32, a fluorine rubber feeder 33 and a die 34, as shown in figure 4. The PBI coated wire 35 is fed into the device from one side and the fluorine rubber coated PBI wire 36 exits from the other side. At the exit zone, the fluorine rubber is immediately reduced in section area by the tractive force of the exiting wire. Immediately afterwards, the fluorine rubber coated PBI wire is stretched at a constant speed.

Conditions for the extrusion may vary according to fluorine-containing rubber materials. In particular, the polymer PTFE requires difficult extrusion conditions, due to its high transition point of 327°C and high molten viscosity of about 10^{11} poises. In this case, as in the case of paste extrusion, the polymer PTFE and oil were emulsion-polymerized to form adhesive particles, then the particles were dried and used.

The extrusion forming consists in three essential steps, preliminary forming, baking and cooling. The preliminary forming is effected at a pressure of around 7 to 10 kg/cm^2. When additives are added to facilitate the extrusion, they are distilled away at 100 to 300°C. The product thus obtained is baked at a temperature above 327°C and cooled to obtain a final product.

Commercially available copolymer FEP melts at 288°C and has a molten viscosity of 6 to 8 X 10^4 poises at 380°C. Characteristically, a tube of copolymer FEP with an appropriate thickness is extruded, drawn to reduce the thickness while covering the PBI-coated wire, then stretched to obtain a final product having the desired FEP coating thickness.

In the case of wires used for hooking up or wire apparatus having a diameter of about 3 mm, these are preferably drawn to obtain a reduction of area of about 100:1, as expressed in a cross-section ratio.

Where the wire has a diameter less than 3 mm and a coating thickness less than 0.75 mm, compressed air or nitrogen gas may preferably be passed over the fluorine rubber coating, thereby pressing the latter onto the PBI coating. The extrusion temperature may be maintained at a low temperature of 320°C to 345°C. The reduction ratio by drawing and stretching may preferably be in the range between 3:1 and 30:1. The product after drawing is rapidly cooled.

To form wire coatings of copolymer PFA, the copolymer may be maintained at 380 to 410°C, then drawn to a reduction ratio of 60:1 to 150:1, preferably about 100:1.

Copolymer ETFE may be extruded at 320 to 350°C, then drawn and stretched to a reduction ratio of 20:1 to 100:

1, preferably about 60:1.

In the case of polymer PVDF, the extrusion temperature may be from 220 to 280°C and the drawing reduction ratio may be from 10:1 to 100:1, preferably about 30:1.

In the case of copolymer ECTFE, the extrusion temperature may be from 250 to 300°C and the drawing reduction ratio may be from 10:1 to 100:1, preferably about 60:1.

As for polymer PCTFE, molding powder or pellets may be used to form wire coatings at an extrusion temperature of 300 to 350°C.

Copolymer EPE may be extruded at a temperature between 360 and 400°C, with a drawing reduction ratio of 20:1 to 100:1, preferably about 100:1.

In the case of polymer PVF, its melting temperature is low at 200°C but very near the decomposition temperature. It may therefore be mixed with a solvent dissolving the polymer PVF at high temperatures, such as 2-pyrrolidone, 2-piperidone, β-propiolactone, etc., then the mixture may be coated on the wire through a wet or dry coating method.

With the exception of polymer PVF, extrusion rate (line speed) may vary from 1 m/min to 1,000 m/min, but preferably between 10m/min and 200 m/min. Polymer PVF apart, extrusion can be effected at a temperature above the melting temperature of fluorine-containing rubbers. It may be chosen appropriately from between 200°C and 350°C.

Particular examples based on the present invention are described hereinafter.

Example 1

A nickel-chromium wire having a diameter of 0.5 mm was soaked or dipped in a varnish solution consisting of 30 parts of PBI molecules and 70 parts of solvent DMA, whereby the wire was applied with the varnish. The varnish was adhered thereto by baking at a line speed of 20 m/min at 350°C. The above procedure was repeated 8 times to obtain a PBI film-coated, nickel-chromium wire.

Copolymer FEP was extruded and adhered around the PBI film-coated wire under the following conditions: drawing reduction ratio 16.3%; drawing balance 1.0 (speed balance between outer and inner tube surfaces when coating a wire by tubing extrusion); extrusion rate 10 m/min; cylinder temperature 260 - 320°C; and then was cooled, whereby a PBI film-coated nickel-chromium wire, further covered with FEP coating was obtained.

Example 2

A nickel-chromium wire having a diameter of 0.5mm was soaked in varnish solution consisting of 30 parts of PBI molecules and 70 parts of solvent DMA, whereby the varnish was applied to the wire. The varnish was adhered thereto by baking at a line speed of 20 m/min at 350°C. The above procedure was repeated 8 times, to obtain a PBI film-coated nickel-chromium wire.

Copolymer PFA was extruded and adhered around the PBI film-coated wire under the following conditions: drawing reduction ratio 70%; drawing balance 1.0; extrusion rate 10 m/min; cylinder temperature 360 to 410°C; and was cooled, whereby a PBI film-coated nickel-chromium wire, further covered with PFA coating, was obtained.

Example 3

A copper wire having a diameter of 0.5mm was soaked in varnish solution consisting of 30 parts of PBI molecules and 70 parts of solvent DMA, the varnish solution further comprising 0.1% (g/ml) of AIBN initiator, whereby the varnish was applied to the wire. The varnish was adhered thereto by baking at a line speed of 50 m/min at 600°C. The above procedure was repeated 8 times, to obtain a PBI film-coated copper wire.

Forming of a PTFE polymer coating by extrusion was effected through 3 main steps consisting of preliminary forming, baking and cooling. The polymer PTFE was emulsion polymerized in oil to form adhesive particles apt to be used for paste extrusion, and dried. The particles thus obtained were extruded for coating at a rate of 10 m/min and extrusion additives were distilled away at 200°C. Then the coated particles were baked at above 327°C and cooled to obtain a PBI film-coated copper wire, further covered with PTFE coating.

Example 4

A nickel-plated copper wire having an external diameter of 0.5mm was soaked in varnish solution consisting of 30 parts of PBI molecules and 70 parts of solvent DMA, the varnish solution further comprising 0.1% (g/ml) of AIBN initiator, whereby the varnish was applied to the wire. The varnish was adhered thereto by baking at a line speed of 50 m/min at 600°C. The above procedure was repeated 8 times to obtain a nickel-plated copper wire covered with a PBI film.

Polymer PTFE was extruded and adhered around the PBI film-coated wire at a rate of 10 m/min and extrusion additives were distilled away at 200°C. Then the polymer was baked at above 327°C and cooled to obtain a nickel

plated copper wire covered with a PBI film and further covered with PTFE coating.

Example 5

A nickel-plated copper wire having an external diameter of 0.5mm was soaked in varnish solution consisting of 30 parts of PBI molecules, 60 parts of DMA solvent and 10 parts of solvent DMSO, the varnish solution further comprising 0.1% (g/ml) of AIBN initiator, whereby the varnish was applied to the wire. Then, the varnish was adhered thereto by baking at a line speed of 20 m/min at 600°C. The above procedure was repeated 8 times to obtain a nickel-plated copper wire covered with a PBI film.

Copolymer PFA was extruded and adhered around the PBI film-coated wire at a rate of 20 m/min at 400°C to obtain a nickel-plated copper wire covered with a PBI film, and further covered with PFA coating.

Example 6

An oxygen-free copper wire having a diameter of 0.36mm was soaked in varnish solution consisting of 20 parts of PBI molecules and 80 parts of solvent DMA, whereby the varnish was applied to the wire. The varnish was adhered thereto by baking at a line speed of 10 m/min at 500°C. The above procedure was repeated 10 times to obtain a PBI coated oxygen-free copper wire.

Copolymer ETFE was extruded and adhered around the PBI-coated wire at a rate of 15 m/min at 330°C to obtain a PBI coated oxygen-free copper wire further covered with ETFE coating.

Example 7

A nickel-plated copper wire having an external diameter of 1.5mm was soaked in varnish solution consisting of 55 parts of PBI molecules and 45 parts of solvent DMA, whereby the varnish was applied to the wire. The varnish was adhered thereto by baking at a line speed of 60 m/min at 700°C. The above procedure was repeated 20 times to obtain a PBI-coated nickel-plated copper wire.

Copolymer PFA was extruded and adhered around the PBI-coated wire at a rate of 30 m/min at 410°C, to obtain a nickel-plated copper wire covered with a PBI film and further with PFA coating.

Example 8

A nickel-plated copper wire having an external diameter 2.5mm was soaked in a varnish solution consisting of 65 parts of PBI molecules and 35 parts of solvent DMA, whereby the varnish was applied to the wire. Then, the varnish was adhered thereto by baking at a line speed of 30 m/min at 600°C. The above procedure was repeated 15 times to obtain a PBI-coated nickel-plated copper wire.

Copolymer ETFE was then extruded and adhered around the PBI-coated wire at a rate of 30 m/min at 340°C to obtain a nickel-plated copper wire covered with a PBI film and further covered with ETFE coating.

Example 9

A nickel-copper alloy wire having a diameter of 1.5mm was soaked in a varnish solution consisting of 55 parts of PBI molecules and 45 parts of DMA solvent, whereby the varnish was applied to the wire. Then, the varnish was adhered thereto by baking at a line speed of 30 m/min at 500°C. The above procedure was repeated 20 times to obtain a PBI-coated alloy wire.

Copolymer ECTFE was extruded and adhered around the PBI coated wire at a rate of 30 m/min at 280°C and with a drawing reduction ratio of 60:1, whereby a nickel-copper alloy wire covered with a PBI film and further covered with ECTFE coating was obtained.

Example 10

A nickel-chromium alloy wire having a diameter of 0.36 mm was soaked in a varnish solution consisting of 20 parts of PBI molecules and 80 parts of DMA solvent, whereby the varnish was applied to the wire. Then, the varnish was adhered thereto by baking at a line speed of 10 m/min at 500°C. The above procedure was repeated 10 times to obtain a PBI-coated alloy wire.

Then, copolymer PFA was extruded and adhered around the PBI-coated wire at a rate of 22 m/min at 405°C to obtain a nickel-chromium alloy wire covered with a PBI film and further covered with PFA coating.

Example 11

An oxygen-free copper wire having a diameter of 0.36 mm was soaked in a varnish solution consisting of 20 parts of PBI molecules and 80 parts of DMA solvent, whereby the varnish was applied to the wire. Then, the varnish was adhered thereto by baking at a line speed of 10 m/min at 500°C. The above procedure was repeated 10 times to obtain a PBI-coated oxygen-free wire.

Then, copolymer EPE was extruded and adhered around the PBI-coated wire at a rate of 30 m/min at 360°C and with a drawing reduction ratio of 100:1, whereby an oxygen-free copper wire covered with a PBI film and further covered with EPE coating was obtained.

Table 1 shows general features of the samples obtained by the foregoing examples.

As is seen in Table 1, all the samples prepared according to the invention show a high heat resistance and a high resistance to dielectric breakdown.

As regards the nickel-chromium wire illustrated in Example 1, ageing testing was effected on PBI and FEP coated wire, as well as wire coated solely with PBI-film, at 300°C for 24 hours under atmospheric air.

Table 2 shows the results of the tests: for the nickel-chromium wire covered merely with the PBI film, dielectric breakdown value (kV) deteriorated from its initial value of 2.1 to 1.9. In the case of the PBI and FEP coated nickel-chromium wire, the FEP coating has been deteriorated. However, when the FEP coating was stripped off, the underlying PBI film showed its initial dielectric breakdown (kV) of 2.1 maintained. Identical results were obtained for Examples 2 and 11.

The examples mentioned above are concerned with non-coated electric wires 11 covered with a PBI film 12 and further with a fluorine-containing rubber coating 13 provided thereon. However, in a variant heat-proof wire 20 shown in Figure 2, the starting wire may be an already coated wire portion 21 comprised of a conductive wire 22 and an insulating coating 23. This wire 21 may be covered with a PBI film 24 and further with a coating 25 comprised of a fluorine-containing rubber.

Moreover, use of the above-mentioned PBI and fluorine-containing rubber films, layers or coatings is not limited to heat-proof electric wires. The structure comprised of a first layer comprised of PBI and a second layer comprised of fluorine-containing rubber disposed thereon may be used more generally as a heat-proof insulating material.

With the heat-proof electric wires or heat proof insulating materials according to the invention, even when they are used in very severe conditions, the PBI film may be prevented from a direct contact with air, whereby advantageous features of the polymer PBI such as heat resistance are retained intact.

Table 1: Dimensions and performance of the samples obtained in Examples 1 to 11

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
PBI-finished wire, outer diameter (mm)	0.516	0.516	0.516	0.516	0.511	0.401
PBI film thickness (mm)	0.008	0.008	0.008	0.008	0.0055	0.0250
Fluorine rubber finished wire, outer diameter (mm)	0.756	0.956	0.756	0.756	0.771	0.701
Fluorine-rubber coating thickness (mm)	0.120	0.220	0.120	0.120	0.130	0.150
PBI finished, dielectric breakdown (kV),initial	2.1	2.1	2.1	2.1	2.2	3.5
Fluorine-rubber finished,dielectric breakdown (kV), initial*	10.0	12.0	10.1	10.0	13.0	14.5
Thermal Shock**	OK	OK	OK	OK	OK	OK
Wear (Use Frequencies) ***	1040	1140	1030	1040	940	950

	Example 7	Example 8	Example 9	Example 10	Example 11
PBI-finished wire, outer diameter (mm)	1.518	2.520	1.519	0.402	0.403
PBI film thickness (mm)	0.009	0.010	0.008	0.0210	0.0215
Fluorine rubber finished wire, outer diameter (mm)	1.858	2.840	1.919	0.640	0.623
Fluorine-rubber coating thickness (mm)	0.170	0.160	0.200	0.119	0.110
PBI finished wire, dielectric breakdown voltage (kV)	2.2	3.5	2.1	3.2	3.2
Fluorine-rubber finished, dielectric breakdown (kV) initial*	15.0	16.0	16.0	13.0	12.0
Thermal Shock**	OK	OK	OK	OK	OK
Wear (Use Frequencies) ***	945	950	845	930	920

* AC, V/1 min

** 220°C X 0.5h after 20% of elongation

*** Load 4N (JASO, D611)

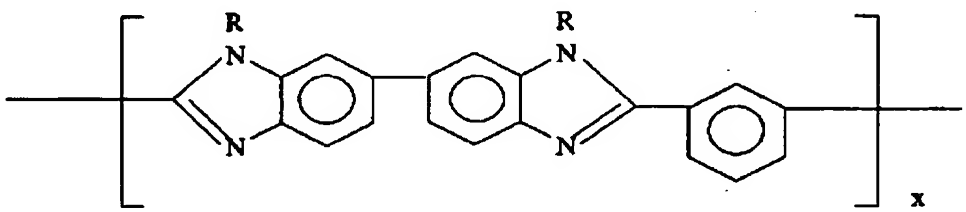
Table 2:

Ageing test effected on the samples (coated Ni-Cr wire) obtained in Example 1		
Dielectric breakdown (kV)	PBI and FEP coat finishing (measured on the PBI film)	PBI film finishing
Before ageing	2.1	2.1
After ageing	2.1	1.9

Claims

1. A heat-proof insulating material for an element containing at least an electrically conductive part, said material comprising a first layer comprised of benzimidazole-based polymer, said layer having a first face adapted to confront said element, and a second face, characterised in that said material further comprises a second layer comprised of a fluorine-containing rubber, said second layer being securely fixed to said second face of the first layer.

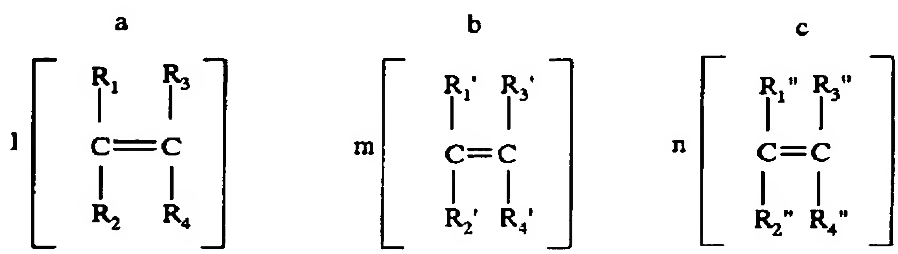
2. A heat-proof insulating material according to claim 1, wherein said first layer comprises a product obtainable by cross-linking a plurality of benzimidazole-based polymers of formula (I):



(I)

where R is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms and x is an integer equal to at least 5 and chosen to yield solvent-soluble polymers.

3. A heat-proof insulating material according to claim 1 or 2, wherein said fluorine-containing rubber comprises a product obtainable by polymerizing a selection of at least one of the monomer groups of a, b and c represented by formula (II):



(II)

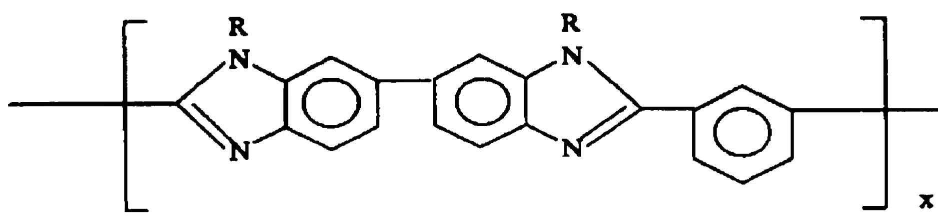
where l, m and n indicate respectively the total number of monomers constituting each group of a, b or c, each of l, m and n ranging from 20 to 200,000; at least one member, chosen from a set consisting of those of R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'' R_3'' and R_4'' which are included in said selection of at least one of the monomer groups, is a fluorine atom, the other members of said set being chosen from the group consisting of a hydrogen atom, a fluorine atom, a chlorine atom, a substituted or non-substituted methyl group and an O-R_5 group, where R_5 is chosen from the group consisting of a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a cyclohexyl group, a cyclohexyl group substituted by lower alkyl groups having 1 to 4 carbon atoms, a hydroxyalkyl group having 1 to 8 carbon atoms, an aminoalkyl group having 1 to 8 carbon atoms, a dialkylaminoalkyl group having 1 to 8 carbon atoms, a glycidyl group, a tetrahydrofuran group, a tetrahydrofuran group substituted by lower alkyl

groups having 1 to 4 carbon atoms, a benzyl group, a group $(-CH_2CH_2-O-)tCH_2CH_2OH$ where t is a positive integer in the range of 1 to 10, and a group R_6-N-R_7 where each of R_6 and R_7 is chosen from the group consisting of a hydrogen atom and an alkyl group having 1 to 4 carbon atoms.

4. A heat proof insulating material according to any one of claims 1 to 3, wherein the element containing at least an electrically conductive part is either an electric wire (11) or an electric wire (22) coated with an insulating layer (23).

5. A heat-proof electric wire (10, 20) comprising a wire portion (11, 21) containing at least an electrically conductive part (11, 22) and a first layer (12, 24) comprised of benzimidazole-based polymer, said layer circumferentially coating said wire portion, characterised in that said heat-proof electric wire further comprises a second layer (13, 25) comprised of a fluorine-containing rubber, said second layer (13, 25) circumferentially coating said first layer (12, 24), said wire portion (11, 21), said first layer (12, 24) and said second layer (13, 25) being securely fixed.

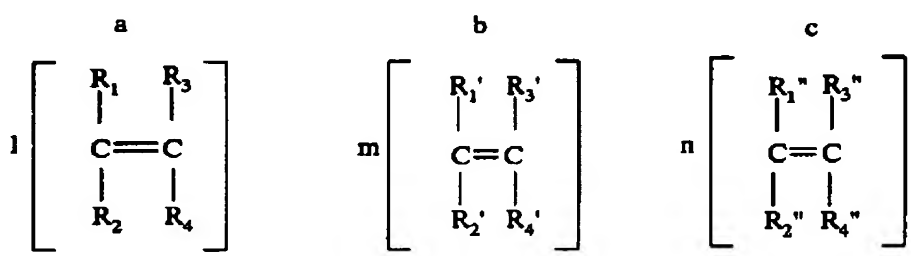
6. A heat-proof electric wire (10, 20) according to claim 5, wherein said first layer (12, 24) comprises a product obtainable by cross-linking a plurality of benzimidazole-based polymers of formula (I)



(I)

where R is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms and x is an integer equal to at least 5 and chosen to yield solvent-soluble polymers.

7. A heat-proof electric wire (10, 20) according to claim 5 or 6, wherein said fluorine-containing rubber comprises a product obtainable by polymerizing a selection of at least one of the monomer groups of a, b and c represented by formula (II):



(II)

where l, m and n indicate respectively the total number of monomers constituting each group of a, b or c, each of l, m and n ranging from 20 to 200,000; at least one member, chosen from a set consisting of those of R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'' R_3'' and R_4'' which are included in said selection of at least one of the monomer groups, is a fluorine atom, the other members of said set being chosen from the group consisting of a hydrogen atom, a fluorine atom, a chlorine atom, a substituted or non-substituted methyl group and an O-R_5, where R_5 is chosen from the group consisting of a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a cyclohexyl group, a cyclohexyl group substituted by lower alkyl groups having 1 to 4 carbon atoms, a hydroxyalkyl group having 1 to 8 carbon atoms, an aminoalkyl group having 1 to 8 carbon atoms, a dialkylaminoalkyl group having 1 to 8 carbon atoms, a glycidyl group, a tetrahydrofuran group, a tetrahydrofuran group substituted by lower alkyl groups having 1 to 4 carbon atoms, a benzyl group, a group $(-CH_2CH_2-O-)tCH_2CH_2OH$ where t is a positive integer in the range of 1 to 10, and a group R_6-N-R_7 where each of R_6 and R_7 is chosen from the group consisting of a hydrogen atom and an alkyl group having 1 to 4 carbon atoms.

8. A heat-proof electric wire (10) according to any one of claims 5 to 7, wherein the wire portion (11) containing at least an electrically conductive part is an electric wire.

9. A heat-proof electric wire (20) according to any one of claims 5 to 7, wherein the wire portion (21) containing at least an electrically conductive part is an electric wire (22) coated with an insulating layer (23).

10. A method for manufacturing a heat-proof insulating material according to any one of claims 1 to 4, said method comprising the steps of:

a) dissolving benzimidazole-based polymers having a low degree of polymerization in a basic solvent, thereby obtaining a varnish solution containing said polymers;
b) adding a radical-polymerization initiating agent to said varnish solution, thereby obtaining a mixture solution;
c) extending said mixture solution into a shape corresponding to the surface of said element to be confronted;
d) baking said mixture solution, whereby said benzimidazole-based polymers are heat cross-linked, thereby forming a first layer having a first face adapted to confront said element and a second face;
e) repeating, where appropriate, steps a) to d) thereby reinforcing said first layer; and
f) coating said second face of the first layer with a second layer comprised of a fluorine-containing rubber so as to be secured on said first layer.

11. A method for manufacturing a heat-proof electric wire (10, 20) according to any one of claims 5 to 9, said method comprising the steps of:

a) dissolving benzimidazole-based polymers having a low degree of polymerization in a basic solvent, thereby obtaining a varnish solution containing said polymers;
b) adding a radical-polymerization initiating agent to said varnish solution, thereby obtaining a mixture solution;
c) applying said mixture solution to the circumferential surface of said wire portion (11, 21);
d) baking said mixture solution, whereby said benzimidazole-based polymers are heat cross-linked, thereby forming a first layer (12, 24) securely on said wire portion (11, 21);
e) repeating, where appropriate, steps a) to d) thereby reinforcing said first layer (12, 24); and
f) coating said first layer (12, 24) with a second layer (13, 25) comprised of a fluorine-containing rubber so as to be secured on said first layer (12, 24).

12. A method for manufacturing a heat-proof electric wire (10, 20) according to claim 11, wherein said coating with a second layer (13, 25) in step f) is effected by extrusion.

13. A method for manufacturing a heat-proof electric wire (10, 20) according to claim 11 or 12, wherein pressurized gas is applied during the extrusion.

14. Use of a heat-proof electric wire (10, 20) according to any one of claims 5 to 9, in an electrical circuitry for an aircraft.

15. Use of a heat-proof electric wire (10, 20) according to any one of claims 5 to 9, in an electrical circuitry for high voltage application.

16. Use of a heat-proof electric wire (10, 20) according to any one of claims 5 to 9, in an electrical circuitry for communication purposes.

17. Use of a heat-proof electric wire (10, 20) according to any one of claims 5 to 9, in an electrical circuitry for an electric heater.

FIG_1

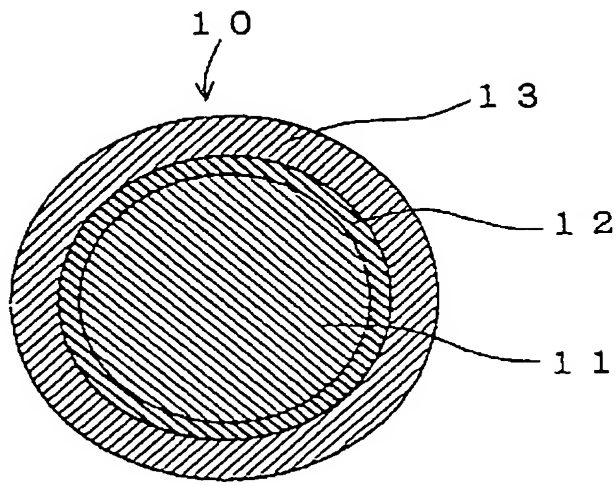


FIG_2

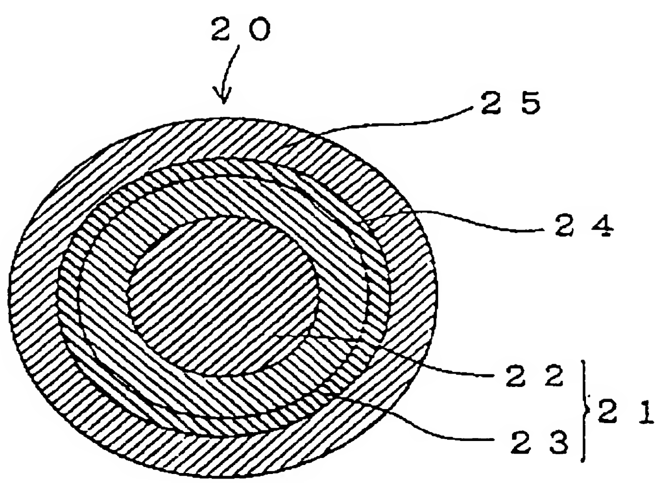


FIG_3

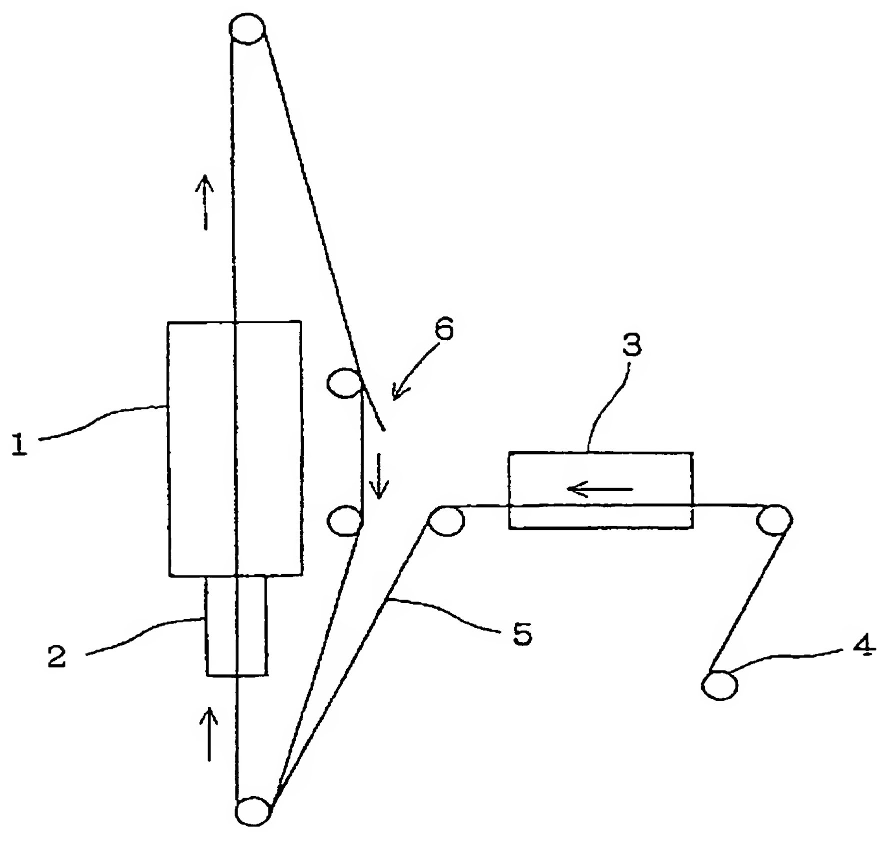


FIG_4